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PROSPECTS IN THE DEVELOPMENT OF ALUMINOSILICATE CERAMICS

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The use of nontraditional raw materials, implementation of fundamentally new methods for mineral material concentration, and introduction of natural additives of complex compositions into aluminosilicate ceramic mixtures opens new opportunities for the development of energy- and resource-saving technologies in ceramic industry.

Special attention has been paid lately to the use of new nontraditional types of mineral materials in the production of aluminosilicate ceramics. One of the main types of such ceramics is porcelain, which in its classical variant is produced from feldspar or pegmatite, quartz sand, and plastic components, namely, refractory white-burning clay and kaolin. However, after transition to the market economy, the porcelain factories in the Russian Federation encountered difficulties, due to the limitations of kaolin supplies from Ukraine and Kazakhstan deposits, and had to look for alternative local varieties of raw materials. The previously performed geological surveys and research in the field of evaluation of new mineral materials prompted a solution for the problems.

Among the topical problems which are important in ensuring stable production of aluminosilicate ceramics are the search for nontraditional raw materials, the development of up-to-date concentration technologies, and study of the effect of various factors on the process of ceramic production based on innovative resource-saving technologies.

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In the last decade, the problem of supply of kaolin to meet the rigorous contemporary requirements for ceramic production has become urgent. Russian manufacturers need about 800 thousand tons of concentrated kaolin per year. Out of this quantity, about 700 thousand tons used to be supplied from Ukraine and Kazakhstan, and only 100 – 105 thousand tons used to be produced in Russia. The need of Russia for kaolin for aluminosilicate ceramics (household and engineering porcelain, electrical and radio engineering) is estimated at 200 – 250 thousand tons per year. The material resources for kaolin in Russia are currently represented by the Kyshtymskoe, Eleninskoe (Chelyabinsk Region), and Chalganovskoe (Amur Region) deposits. Concentration enterprises supply around 80 thousand tons of concentrated kaolin per year, which does not cover even one-tenth of the demand in this type of mineral materials.

Russia possesses considerable surveyed resources of kaolin materials. Promising deposits are situated in the South Ural. One of the deposits best prepared for mining is the Zhuravlinyi Log deposit (Chelyabinsk Region). This is a source of high-quality kaolin, capable of fully satisfying the need in this material and making it possible to discard the supplies of kaolin from Ukrainian deposits.

By their genesis, the kaolins from Zhuravlinyi Log are alluvial (primary) materials. According to the data of N. F. Solodkii [1], the mineral composition of natural kaolin is represented by kaolinite (45%), quartz sand (42%), potassium feldspar (5%), and other minerals (8%). Table 1 shows the chemical composition of the kaolin from Zhuravlinyi Log de-

TABLE 1

Kaolin	Mass content, %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	calcination loss
				Zhuravlinyi Log deposit					
Raw kaolin	68.98	20.92	0.48	0.55	0.80	0.58	0.75	0.10	7.34
Concentrated	47.44	36.20	0.49	0.57	0.82	0.50	0.41	0.10	13.47
				Kyshtymskoe deposit					
Concentrated	46.08	36.80	1.01	0.66	0.76	0.61	0.99	0.26	12.83
				Prosyanovskoe deposit					
Concentrated	44.36	36.60	0.81	0.63	0.52	0.38	0.50	0.16	14.09

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posit and, for reference purposes, the chemical composition of kaolins from some other operated deposits.

By their chemical and mineralogical compositions, the kaolins from Zhuravlinyi Log are high-quality mineral materials characterized by a low content of pigment oxides, i.e., 0.22 – 0.70% Fe_2O_3 and 0.20 – 0.56% TiO_2. The kaolin is distinguished by a high content of finely dispersed particles (78.8% below 5 μm, and up to 54% below 1 μm) and the presence of mica in the form of sericite inclusions in these particles. The granulometric compositions of the kaolins from Zhuravlinyi Log and other operated deposits are given in Table 2.

Based on the elasticity index, the kaolins concentrated by the electrolyte-free method belong to groups 1 and 2; they have high threshold of structure formation values (1.31 – 1.38) and satisfactory fluidity.

It is established that kaolin from Zhuravlinyi Log should be regarded as one of the main material components for the production of aluminoboron-silicate ceramic mixtures, which can be processed by molding and by casting in gypsum molds.

The microstructure of experimental and production porcelain specimens fired in an industrial furnace 93 m long (Table 3), as well as their physicotechnical properties (Table 4), testify to their satisfactory quality and the possibility of using Zhuravlinyi Log kaolin in the production of household porcelain.

In the production conditions of the Yuzhnouralskii Porcelain Factory (Chelyabinsk Region), for the first time in our country, the Prosyanovskoe kaolin was replaced by the Zhuravlinyi Log raw kaolin. The technology of the porcelain mixture production did not undergo significant changes.

As a consequence of studies carried out at the Isolyator factory (Moscow), the expediency of using this kaolin in production of electrotechnical porcelain was corroborated [2].

However, in developing the Ural deposits of mineral materials, a number of problems need to be solved, which are related to developing optimum schemes of material concentration and the technologies for molding articles from aluminosilicate ceramic mixtures based on these kaolins, which would be determined by the specifics of their mineral and granulometric compositions. Special attention should be paid to researching fundamentally new concentration methods, including complex techniques of microbiological and chemical effects, as well as studying the effect of different additives on the casting properties of slips.

The results of testing the methods of wet and dry concentration of Zhuravlinyi Log kaolin indicated that the concentrated kaolin does not differ from Prosyanovskoe kaolin and meets the requirements of GOST 21286–82.

One of the pressing current problems is the development of resource-saving technologies in production of aluminosilicate ceramics. To solve this problem, a series of studies was carried out whose primary purpose was to decrease the temperature of ceramic product firing.

TABLE 2

Kaolin	Content, %, of fractions with grain size, mm				
	0.05	0.05 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001
Kyshtymskoe	5.43	19.96	15.53	28.97	35.11
Zhuravlinyi Log	18.80	15.40	17.10	29.30	49.50
Eleninskoe	10.59	34.69	16.07	21.66	16.99
Prosyanovskoe	1.57	13.52	5.61	27.24	42.06

TABLE 3

Parameter	Porcelain	
	industrial	experimental
Phase composition of porcelain, %:		
mullite	22.00	29.00
glass-mullite component	78.80	80.72
residual quartz	18.35	16.27
pores	2.85	3.01
Mullite to quartz content ratio	1.198	1.780
Mullite needle-shaped crystals:		
length, μm	5 – 20 (10 – 15 prevails)	5 – 30 (20 prevails)
presentation	Thick and loosely woven mesh	
Edge thickness of the fusion zone of residual quartz grains, μm	2.0 – 2.5 (rarely 3.0)	2.2 – 2.9 (in the corners up to 3.5)
Refractive index:		
porcelain vitreous phase	1.523 – 1.526	1.519
glaze	1.501	1.503
Glaze layer thickness, μm	240 – 300	210 – 270
Type of stresses in glaze	Compression	

TABLE 4

Parameter	Porcelain	
	industrial	experimental
Firing duration, h	38	38
Porcelain whiteness, %	56 – 61	63 – 65
Water absorption, %	0.03	0.02
Translucence, %	1.29	1.48
Glaze luster, %	62	63
Strength, MPa:		
compressive	382.0	417.0
bending	70.8	89.6
Glaze microhardness, MPa	67.2	69.7
Thermal resistance, number of thermal cycles	More than 10	
Density, g/cm^3	2.39	2.43

As shown by numerous studies performed with different degrees of detail of the physicochemical analysis of aluminosilicate ceramic production, using contemporary methods based on the effect of mineralizers on the structure formation of aluminosilicate ceramics and their properties, the most

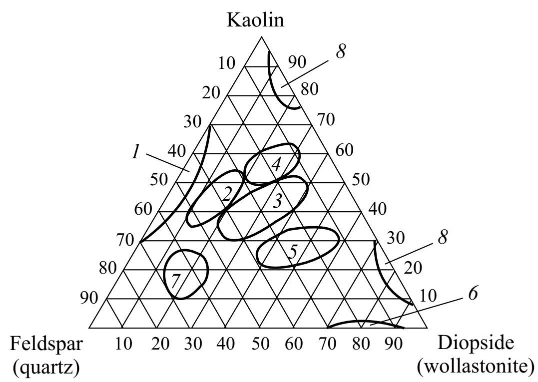

Fig. 1. Phase diagram of mixture compositions in the kaolin – feldspar – diopside system: *1*) hard porcelain; *2*) low-temperature porcelain; *3*) heat-resistant porcelain; *4*) faience, half-porcelain; *5*) porcelain (dry-press molding); *6*) porcelain (hot injection molding); *7*) glaze; *8*) engobe.

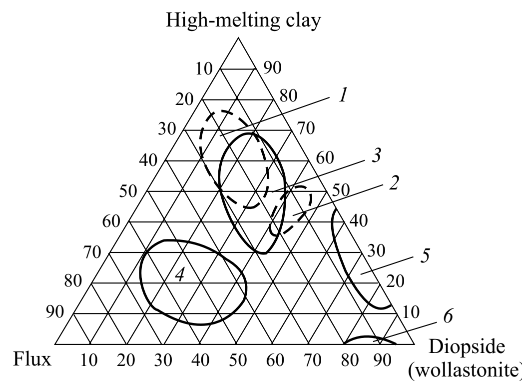

Fig. 2. Phase diagram of mixture composition in the high-melting clay – diopside – flux system: *1*) faience, majolica; *2*) heat-resistant stone product; *3*) ceramic tile; *4*) glaze; *5*) engobe; *6*) household ceramics (hot injection molding).

promising method is the introduction of complex additives into ceramic mixtures, including additives represented by natural minerals of complex composition. It should be noted that the theoretical grounds for selecting mineralizing additives were phase diagrams of complex systems [3 – 7], which had been previously used to a very limited extent in the development of compositions for new ceramic materials.

Thus, the phase diagram of the $MgO – B_2O_3 – SiO_2$ system was used to demonstrate that introduction of a third component, namely, a mineralizer into a binary system decreases the melt viscosity and the temperature of ceramic material formation, and significantly extends the structure formation range.

The summarized experimental data obtained in studying various systems serve to develop the concept of phase diagrams of complex systems (oxide, oxycarbide, carbide and other oxygen-free systems), as well as the concept of their use in the practice of ceramic materials.

The role of mineralizing additives was considered in several papers in different aspects. The results of these studies were corroborated in some papers published in recent years, in particular the paper by V. M. Pogrebenkov [7] which systematized the data on successful use of calcium-magnesium-bearing materials in aluminosilicate ceramic technology.

With respect to additives of complex natural minerals, the effect of diopside, wollastonite, talc, dolomite, magne-

TABLE 5

Type of ceramics	Amount of melt, %	Additive		Role of the additive
		component	content, %	
High-temperature ceramics (t_f = 1200 – 1350°C)	> 50	Diopside Wollastonite Tremolite	< 5 < 5 < 5	Melt modification, intensification of mullite formation
Porcelain (hard, low-temperature, half-porcelain)		Talc	10 – 50	Formation of new phase: anorthite, cordierite, mullite
Medium-temperature ceramics (t_f = 1050 – 1150°C) Faience Majolica	25 – 35	Diopside Wollastonite	15 – 35 15 – 35	Formation of new phases (anorthite) with substantial preservation of the base
Low-temperature ceramics (t_f = 950 – 1050°C)	20 – 30	Diopside Wollastonite	20 – 60 20 – 60	Preservation of crystal base with subordinated phase formation of anorthite
Ceramic tiles		Zeolite	< 20 > 20	Flux Formation of porous material
Pigments (t_f = 1000 – 1250°C)	–	Diopside Wollastonite Talc Tremolite Zeolite	Up to 95 ″ ″ ″ ″	Formation of crystalline base of the pigment*

* Diopside → diopside; wollastonite → anorthite, diopside; talc → diopside, enstatite, forsterite; tremolite → diopside; zeolite → clinoptilolite.

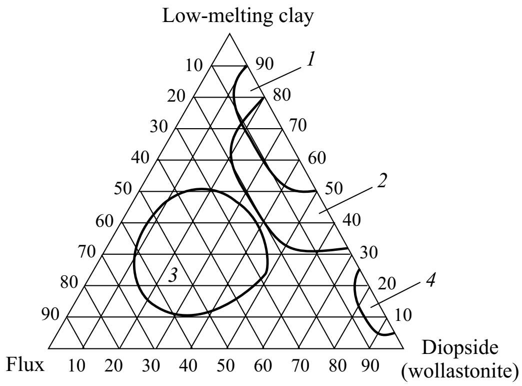

Fig. 3. Phase diagram of mixture compositions in the low-melting clay – diopside – flux system: *1*) majolica; *2*) ceramic tile; *3*) glaze; *4*) engobe.

site, calcite, etc. (up to 5%), on the sinterability, structure, and properties of porcelain was investigated. Prior to this, Yu. T. Platov [8] et al. had performed studies in the same area (Table 5).

Figures 1 – 3 show phase diagrams of various-purpose mixtures containing diopside, and Tables 6 and 7 indicate experimental compositions and properties of low-temperature porcelain.

The introduction of 10% diopside has the most favorable effect. The firing temperature decreases by 20%, the whiteness increases by 5%, and the bending strength by 30 MPa. An additional introduction of concentrated datolite (2.5 and 3.5%, respectively) to mixtures containing 15 and 20% diopside brings the firing temperature down to 1160°C. As the diopside content grows, a transition from the quartz-mullite crystalline phase in the standard mixture to the quartz-anorthite phase is observed upon addition of 15 – 20% diopside. The use of diopside is especially effective in the production of low-temperature porcelain articles fired in slot-type furnaces with precise temperature control; therefore, a certain narrowing of the sintered state interval does not create substantial obstacles to the firing process.

The developed crystalline phase and the high purity of the Slyudyanskoe diopside made it possible to use it in mixtures for the production of porcelain from thermoplastic slip by hot injection molding. Feldspar, glass cullet, and broken household porcelain were tested as fluxes. The best results were observed in a mixture with 85% diopside and 15% feldspar.

A successful approach to the development of resource-saving technologies is the introduction of nontraditional fluxes (perlite, obsidian, and other rocks) in ceramic mixture compositions. It was demonstrated [3] that the introduction of perlite, which is a volcanic siliceous rock, into a mixture makes it possible to obtain aluminosilicate ceramic materials whose intense sintering starts around 1000°C.

As a consequence of studying the structure of perlite-based materials it was found that their crystalline phase is represented by agglomerates of mullite crystals chaotically distributed in the vitreous phase of aluminosilicate ceramics, which determines their sufficiently high physical and technical parameters. The compositions of perlite-bearing mixtures and their sintering temperatures are indicated in Table 8.

In the course of thermal treatment of ceramic materials, a high content of silicon dioxide in perlite, as well as enriching the melt with siliceous compounds from the cullet and the argillaceous component, determine the stability of high viscosity of the forming material within the temperature interval of 900 – 1000°C. The properties of ceramic materials based on perlite are presented in Table 9.

It can be seen that perlite-bearing materials mostly sinter at temperatures 1050 – 1120°C. An increase in the amount of fluxes and the introduction of

TABLE 6

Low-temperature porcelain (NF)	Mass content, %								
	Troshkovskoe clay	Veselovskoe clay	Prosyanovskoe kaolin	feldspar (KPShK)	dolomite	diopside	alumina	broken porcelain	concentrated datolite
NF0	7.0	5.0	29.0	48.0	2.5	–	3.5	5.0	–
NF1	7.0	5.0	29.0	40.5	–	10.0	3.5	5.0	–
NF2	7.0	5.0	29.0	35.5	–	15.0	3.5	5.0	–
NF3	7.0	5.0	29.0	33.0	–	15.0	3.5	5.0	2.5
NF4	7.0	5.0	29.0	27.0	–	20.0	3.5	5.0	3.5

TABLE 7

Parameter	Low-temperature porcelain (NF)				
	NF0	NF1	NF2	NF3	NF4
Firing shrinkage, %	11.9	12.1	10.9	12.2	11.3
Water absorption, %	0.8	0.3	3.0	0.4	0.3
Bending strength, MPa	81.8	110.5	77.1	84.4	92.3
TCLE, $10^{-6}\,°C^{-1}$	5.8	6.4	5.9	6.1	5.9
Whiteness, %	46	51	52	51	53
Heat resistance, °C	175	195	170	175	175

TABLE 8

Mixture	Batch composition of mixture, wt.%				Sintering temperature, °C
	refractory clay from Veselovskoe deposit	perlite from Aragatskoe deposit	broken glazed ceramics	glass cullet	
P1	35	50	–	15	1050
P2	40	50	2	8	1060
P3	42	40	8	10	1080
P4	40	47	5	8	1060
P5	45	55	–	–	1120
P6	38	55	7	–	1120

TABLE 9

Parameter	Material						
	P1	P2	P3	P4	P5	P6	P7
Firing temperature, °C	1050	1050	1050	1080	1120	1120	1020
Total shrinkage, %:							
at temperature 750°C	4.8	4.7	4.7	6.3	4.7	6.3	4.9
after second firing	14.1	14.6	14.4	15.0	14.5	15.0	13.6
Water absorption, %:							
at temperature 750°C	17.2	17.1	17.6	17.5	17.6	17.1	17.8
after second firing	0.1	0.08	0.6	0.09	1.2	0.43	0.2
Bending strength of fired material, MPa	70 – 71	82 – 83	52 – 53	77 – 78	78 – 79	80 – 81	52 – 54

a certain amount of glass cullet (mixtures P1 – P3, P7) provide for sintering at lower temperatures.

Since intense sintering of perlite-bearing materials starts at temperatures above 1000°C, due to the formation of a substantial quantity of the liquid phase, the firing of articles is terminated at early stages of sintering.

The technology of low-temperature ceramics is successfully implemented at three enterprises in Georgia, where floor tiles and various household ceramic articles are manufactured from perlite-bearing mixtures.

It can be stated that the expansion of material resources toward the use of nontraditional materials and the development and industrial implementation of fundamentally new methods for concentration of mineral materials, as well as the introduction of natural additives of complex compositions into aluminosilicate ceramic mixtures, open new prospects for the development of energy- and resource-saving technologies in ceramic industry.

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